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Density functional theory study of the adsorption and incorporation of Sc and Y on the AlN(0001) surface

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ABSTRACT

Density functional theory (DFT) calculations were carried out in order to study the adsorption and incorporation of scandium and yttrium atoms on the AlN(0001) surface aiming to gain insight into epitaxial growth of $Sc_xAl_{1-x}N$ and $Y_xAl_{1-x}N$ layers on AlN. The adsorption energy, geometry, formation energy, band structure and density of states of Sc (and Y) adatom/AlN(0001) systems are calculated. The calculations showed that the interaction between Sc (and Y) adatom and the AlN(0001) surface is strong (~ 3.9 eV) and it prefers to adsorb on N-top site (T4). However, formation energy calculations reveal that the incorporation of Sc and Y atoms in the Al-substitutional site is energetically more favorable compared with the adsorption on the top layers, which can be attributed to the lower enthalpy of formation of ScN and YN with respect to that of AlN. The results also suggest that the Sc and Y atoms prefer to incorporate in top AlN surface layers. At full coverage, calculations show the formation of metallic Sc_xN and $Y_xAl_{1-x}N$ layers on the AlN polar surface over the entire range of Al chemical potentials, in agreement with experimental observations. In addition, we found that for high coverage Sc atoms couple ferromagnetically in the Al-substitutional sites on the AlN(0001) surface.

1. Introduction

Wide direct band-gap nitride semiconductors have attained technological interest because of their applications in manufacturing optoelectronic devices spanning the blue and ultraviolet region of the optical spectrum. The 2014 Nobel Prize for physics was awarded to Scientists Isamu Akasaki, Hiroshi Amano and Shuji Nakamura for the invention of blue light emitting diodes [1,2]. Among these semiconductors with large and direct band gaps, the aluminum nitride (AlN), with a band-gap of 6.2 eV [3] in the wurtzite phase, has been widely studied both theoretically and experimentally [4–7]. AlN is a semiconductor of high chemical and thermal stability, hard and partially ionic [8]. It also displays a variety of applications such as sensors, passive barrier layers, high-frequency acoustic wave devices, high-temperature windows, and dielectric optical enhancement layers in magneto-optic multilayer structures [9]. Bulk AlN single crystal can also be used as substrate material for growth of many III-nitride structures [10–12] because of the good structural, thermal and chemical compatibility among these materials.

Over the last decade, transition metal doped wide band gap semiconductors such as AlN and GaN have attracted scientific interest because of their potential applications in spintronics [13–15]. It is desirable doping conventional compound semiconductors with nonmagnetic transition metals in order to avoid problems of precipitates in the form of clusters or secondary phase formations in the host semiconductor which could happen when doping semiconductors with magnetic transition metals [16–18]. Recently, W. Lei et al. have experimentally shown that yttrium (Y) doped AlN nanorods exhibit room-temperature ferromagnetism [19]. From this study, the authors infer that the Al vacancy could induce a high spin polarization in AlN:Y systems. In addition, W. Lei et al. found that scandium (Sc) is a potential nonmagnetic dopant for preparing nanostructured scandium magnetic semiconductors by direct current arc discharge plasma method [20]. They confirm the existence of ferromagnetic ordering at room-temperature in AlN:Sc hierarchical nanostructures and suggest that further investigations must be carried out in order to determine the origin of the ferromagnetic behavior of AlN:Sc nanostructures. In addition, controlling the crystallography and shape of AlN-based nanostructures is a key step towards extending their use in applications. Whilst AlN:Sc and AlN:Y nanorods have been fabricated, precise control over the specific surface facets and tailoring of polar growth directions still demands a significant refinement.

In order to clarify how Sc and Y atoms affects the AlN surface and establish the origin of the magnetism in Sc-doped and Y-doped AlN, we have comparatively studied the structural and electronic properties for a single Sc and Y atoms adsorbed and incorporated on the AlN(0001) surface by density functional

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theory calculations. It has been chosen the [0001] direction because previous investigations of nitride growth on substrates state that epitaxial films grown in the [0001] direction is preferred instead of any of the others [21–24]. Furthermore, this study will yield essential knowledge to understand and control the epitaxial growth process of $Sc_xAl_{1-x}N$ and $Y_xAl_{1-x}N$ films on the AlN(0001) surface.

2. Computational methods

All calculations were performed using the `quantum-espresso` simulation package [25], which performs fully self-consistent spin Density Functional Theory (DFT) calculations to solve the Kohn-Sham equations. Exchange and correlation effects were treated with generalized gradient approximation (GGA) implemented in the Perdew-Burke-Ernzerhof functional [26]. Ultrasoft pseudopotentials were employed to represent core-valence electron interactions [27], wherein the *d* states for the Sc and Y atoms were included as valence electrons. The electronic wavefunctions were expanded as a linear combination of plane waves, and truncated to include only plane waves with kinetic energies less than 50 Ry (500 Ry for the charge-density cutoff). A Γ centered grid of $5\times5\times1$ *k*-point was used to sample the irreducible Brillouin zone in the Monkhorst-Pack special scheme [28]. Methfessel-Paxton smearing technique with a smearing width of 0.02 Ry was adopted [29]. These parameters ensure a convergence better than 10 meV for the total energy.

AlN polar surfaces were modeled using the supercell approach, where periodic boundary conditions are applied to a central cell, so that it is repeated periodically throughout three-dimensional space. An asymmetric slab of four AlN bilayers was used for the AlN(0001) surface. A vacuum region of ~15 Å was included in the direction orthogonal to the surfaces. The two lowest AlN bilayers were fixed in the bulk configuration, while the two uppermost AlN bilayers as well as the Sc and Y atoms were allowed to relax. The dangling bonds at the bottom layer were saturated with pseudo-hydrogen atoms, each one with a fractional charge of 0.75 *e* to prevent unphysical charge transfer between the top and bottom slab surfaces. The structural optimizations were terminated when the magnitude of the force acting on each ion was less than 1 m Ry/bohr.

3. Results and discussion

Aluminum nitride bulk calculation was carried out using a wurtzite (hexagonal) unit cell with two lattice parameters *a* and *c*, and an internal parameter *u*. The geometry optimization was performed to vary both the lattices parameters and relaxing the internal parameter in order to minimize the overall energy. The calculated lattice parameters obtained for AlN were $a=3.117\text{Å}$, $c=4.997\text{Å}$, and the internal parameter $u=0.382$, which are slightly higher than experimental values $a=3.112\text{Å}$, $c=4.979\text{Å}$ and $u=0.382$ [30]. Lattice parameters *a* and *c* were overestimated in 0.2 and 0.4%, respectively. The calculated lattice parameters for AlN were used to build the AlN(0001) asymmetric-slab supercell. The initial atomic positions were determined by minimizing the total energy of the clean AlN surface.

For the adsorption study of scandium and yttrium atoms on AlN(0001), different Sc and Y adatom positions were examined to establish the most stable structure. We selected three special high-symmetry points on the clean AlN(0001) surface, as shown in Fig. 1. A Sc and Y atom were located in these positions (H3, T4 and T1) and then the atomic positions were allowed to relax. For Sc and Y incorporation processes, a large number of configurations

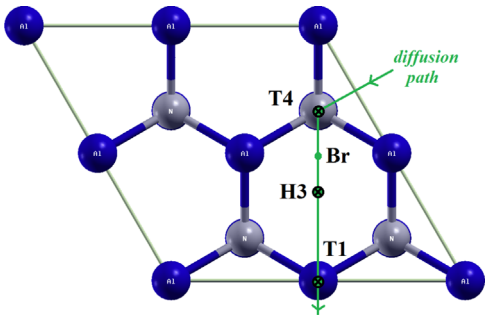

Fig. 1. Ball and stick model of AlN(0001) surface. The blue balls represent Al atoms and the gray balls represent N atoms. Top view of the adsorption sites: top (T4), top (T1), hollow (H3) and bridge (Br). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Calculated parameters for Sc and Y adsorption and incorporation on AlN (0001) surface. Surface coverage Θ, bond lengths $d_{Sc-N}, d_{Sc-Al}, d_{Y-N}, d_{Y-Al}(\text{Å})$, adsorption energy E_{ads} *eV* , formation energy E_f eV and total magnetic moment TMM (μ_B).

	Θ_{Sc}	d_{Sc-Al}	d_{Sc-N}	E_{ads}	E_f	TMM
Sc-H3	0.25	2.891	3.519	−3.426	0.689	0.00
Sc-T4	0.25	2.834	2.974	−3.845	0.271	0.00
(1/0/0/)	0.25	3.135	2.067	–	−1.151	0.00
(0/1/0/)	0.25	3.130	2.052	–	−0.279	0.00
(2/0/0/)	0.50	3.054	2.043	–	−1.973	0.00
(1/1/0/)	0.50	3.120	2.040	–	−0.950	0.00
(3/0/0/)	0.75	3.054	2.024	–	−2.343	1.01
(2/1/0/)	0.75	2.974	2.033	–	−1.886	1.06
(3/1/0/)	1.00	2.986	2.035	–	−2.355	1.01
(2/2/0/)	1.00	3.031	2.024	–	−2.342	1.10
(3/3/0/)	1.50	3.076	2.006	–	−2.317	0.99
(4/3/0/)	1.75	3.123	2.007	–	−1.932	1.83
(4/4/0/)	2.00	3.292	2.002	–	−1.706	2.27
	Θ_Y	d_{Y-Al}	d_{Y-N}	E_{ads}	E_f	TMM
Y-H3	0.25	3.031	3.653	−3.612	0.573	0.00
Y-T4	0.25	2.981	3.134	−4.030	0.155	0.00
(1/0/0/)	0.25	3.197	2.231	–	−1.120	0.00
(0/1/0/)	0.25	3.155	2.171	–	0.431	0.00
(2/0/0/)	0.50	3.150	2.165	–	−0.999	0.00
(1/1/0/)	0.50	3.134	2.175	–	0.289	0.00
(2/1/0/)	0.75	3.071	2.168	–	−0.036	0.00
(3/0/0/)	0.75	3.179	2.144	–	0.134	0.00
(2/2/0/)	1.00	3.024	2.143	–	0.431	0.00
(3/1/0/)	1.00	3.056	2.134	–	0.716	0.00
(4/2/0/)	1.50	3.009	2.090	–	1.726	0.00
(4/3/0/)	1.75	3.148	2.078	–	5.982	0.00
(4/4/0/)	2.00	3.475	2.109	–	8.464	0.00

with different amounts of Sc and Y atoms in substitutional Al and N sites were studied and labeled as $(l_1/l_2/l_3/)$, where l_1, l_2 and l_3 are the numbers of Sc (or Y) atoms in the first, second and third bilayer, respectively, beginning from the top surface layer. For instance, (4/0/0/) configuration represents four Sc (or Y) atoms incorporated in the first bilayer (1.0 ML), and not atoms present in the deeper AlN bilayers.

Table 1 shows the structural changes induced by Sc and Y adsorption on the AlN (0001) surface, after relaxation. In Table 1 are only registered the most stable final adsorption configurations for the Sc and Y atom on the AlN polar surfaces. The adsorption energies E_{ads} were calculated as the difference between the total energy of the AlN(0001) slab with adsorbed Sc (or Y) atom and the sum of the total energies of the clean surface and the isolated Sc (and Y) atom. Furthermore, the bond lengths $d_{Sc-Al}, d_{Sc-N}, d_{Y-Al}$ and d_{Y-N} were calculated from the average distance between Sc (or Y) atoms and Al-N surface atoms. The E_{ads} calculated values,